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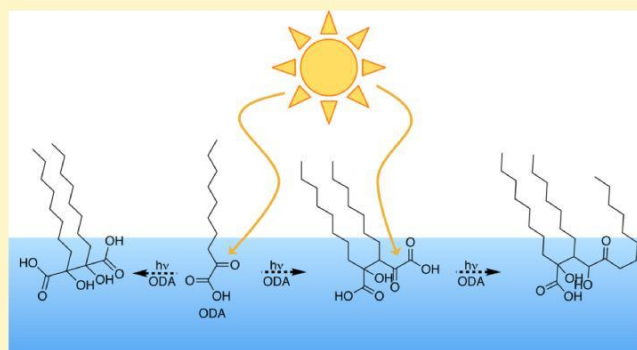
Photochemical Synthesis of Oligomeric Amphiphiles from Alkyl Oxoacids in Aqueous Environments

Rebecca J. Rapf,^{†,‡} Russell J. Perkins,^{†,‡} Haishen Yang,^{†,‡} Garret M. Miyake,^{†,§} Barry K. Carpenter,^{||} and Veronica Vaida^{*,†,‡}

[†]Department of Chemistry and Biochemistry, [‡]Cooperative Institute for Research in Environmental Sciences, and [§]Materials Science and Engineering Program, University of Colorado Boulder, Boulder, Colorado 80309, United States

^{||}School of Chemistry and the Physical Organic Chemistry Centre, Cardiff University, Cardiff CF10 3AT, United Kingdom

ABSTRACT: The aqueous phase photochemistry of a series of amphiphilic α -keto acids with differing linear alkyl chain lengths was investigated, demonstrating the ability of sunlight-initiated reactions to build molecular complexity under environmentally relevant conditions. We show that the photochemical reaction mechanisms for α -keto acids in aqueous solution are robust and generalizable across alkyl chain lengths. The organic radicals generated during photolysis are indiscriminate, leading to a large mixture of photoproducts that are observed using high-resolution electrospray ionization mass spectrometry, but these products are identifiable following literature photochemical mechanisms. The alkyl oxoacids under study here can undergo a Norrish Type II



reaction to generate pyruvic acid, increasing the diversity of observed photoproducts. The major products of this photochemistry are covalently bonded dimers and trimers of the starting oxoacids, many of which are multi-tailed lipids. The properties of these oligomers are discussed, including their spontaneous self-assembly into aggregates.

INTRODUCTION

The reactivity and synthesis of lipid-like molecules are of interest for environmental chemistry of both the modern and ancient Earth.^{1–9} In the environment, lipid-like molecules selectively partition to air–water interfaces. Sunlight can drive photoinitiated chemistry of organic species at air–water interfaces, such as the sea-surface microlayer (SML).^{10–16} The SML contains high concentrations of amphiphilic organic molecules and, as the boundary layer between the ocean and atmosphere, connects processes at the sea surface with the atmosphere, including the generation of sea spray aerosol. Recent work suggests that oligomers formed from aqueous phase photochemistry of small organic molecules may contribute significantly to the formation and development of secondary organic aerosol (SOA).^{17–25} The surface-active molecules found in the SML are often biological in

origin, but abiotic photochemical sources may be additional, important contributors.^{11,12,23,28–30} Such sunlight-driven reactions are critical in the understanding of the formation of marine-derived primary organic aerosol and SOA,^{31–37} influencing visibility, human health, cloud formation,

and radiative forcing.

The present study investigates the photochemistry of a series of amphiphilic α -keto acids, also known as^{17,19,38–46} 2-oxoacids that will be referred to as oxoacids here, with varying alkyl tail lengths. Such oxoacids have been identified at the ocean surface and are

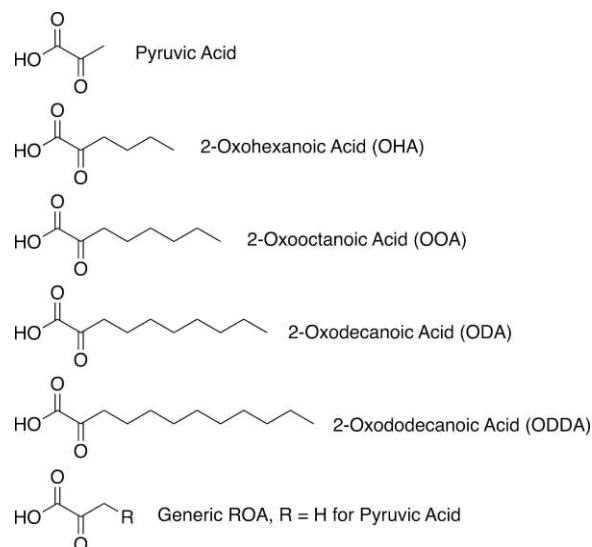
significant contributors to the environment today^{14,47,48} and likely would have been found on the early Earth.^{49–52} In this work, we describe the general photochemical mechanism for α -keto acids in aqueous solution under acidic conditions, investigating the effect of the alkyl tail length. By demonstrating this mechanistic understanding of the photochemistry of α -keto acids, we show its generalizability across a class of molecules, widening the library of compounds whose photolysis may contribute to the reactivity found in natural environments.

Previously, the photochemistry of the simplest of α -keto acid, pyruvic acid, has been studied in detail in both the gas^{53–60} and

the aqueous phases,^{48,70–78} because of its atmospheric relevance. Like all α -keto acids, pyruvic acid absorbs light in the near-UV within the spectral range of wavelengths^{28,61–69} of sunlight that are available near the surface of the Earth, and direct photolysis is its main atmospheric sink.^{28,57,58} In the aqueous phase, pyruvic acid readily forms oligomers,^{28,63,64,67,79} including in atmospherically relevant, multiphase studies using an environmental simulation chamber.⁶⁸ These covalently bonded dimers and trimers⁸⁰ are generated in relatively high yields from the recombination of photochemically generated organic radicals and are the major observed photoproducts, especially under oxygen-limited reaction conditions.^{28,63,64,67}

In this study, we examine the photoreactivity in aqueous solution at unadjusted pH of four oxoacids (shown in Chart 1)

Chart 1. Structures of Pyruvic Acid and the Four Oxoacids Studied in This Investigation: 2-Oxohexanoic Acid (OHA), 2-Oxooctanoic Acid (OOA), 2-Oxodecanoic Acid (ODA), and 2-Oxododecanoic Acid (ODDA)



with differing saturated, linear alkyl chains, ranging from the four-carbon butyl tail of 2-oxohexanoic acid to the 10-carbon decyl tail of 2-oxododecanoic acid, and compare these results to the known photochemistry of pyruvic acid, possessing a single-carbon methyl tail. We demonstrate that the pyruvic acid photochemical mechanism is transferrable to molecules with the same reactive functional groups, including those compounds with longer alkyl chains that are relevant to the generation of large, surface-active oligomer species that contribute to the SML. These longer-tailed species also follow additional reactive pathways that are not available to the short-tailed pyruvic acid, increasing the complexity of the mixture of photoproducts generated.

Organic photochemistry, as investigated here, also has significant implications for the study of prebiotic chemical evolution and the generation of biomolecules in the absence of enzymatic assistance,⁴ including the abiotic synthesis of lipid molecules.^{4,52} The synthesis of lipid molecules is interesting, not only because of the formation of a carbon-carbon bond in the absence of biology, but also because of the importance of such molecules in the formation of membranous enclosures. Such enclosures form the basis for protocells and are recognized as vital to developing and sustaining life.^{9,81-87}

EXPERIMENTAL SECTION

2-Oxooctanoic acid (OOA, ≥99.0%, Sigma-Aldrich) was diluted with 18.2 MΩ water (3 ppb TOC) to obtain solutions of 6, 3, and 1 mM and sonicated until fully dissolved. Solutions were filtered before use with a 0.1 μm syringe filter (MillexV). The remaining alkyl oxoacids (referred to generically as ROA), 2-oxohexanoic acid (OHA), 2-oxodecanoic acid (ODA), and 2-oxododecanoic acid (ODDA), were synthesized as described below and diluted in the same manner as OOA to obtain 1 mM solutions. 6 mM OHA and 3 mM ODA solutions were also used. Solutions consisting of mixtures of 1:1 OOA:ODA were obtained in the same manner with either 3 or 1.5 mM concentrations of each oxoacid, giving a total amphiphile concentration of either 6 or 3 mM, respectively. It has recently been

suggested that solutions of OOA at concentrations similar to those used here can result in the formation of vesicles.⁸⁸ We do not observe this under our experimental procedure. Dynamic light scattering of the pre-photolysis solutions (OHA, OOA, ODA, and OOA/ODA) confirmed that aggregates were not detectable in our solutions prior to irradiation.

The solutions were used without adjustment from their natural pH, meaning all photolyses were conducted under acidic conditions. There is a slight variance in the pH of the solutions as a function of the concentration of ROA. For example, the 6 mM OOA solutions are pH ≈ 2.5, increasing slightly to ~2.8 and ~3.3 for the solutions at 3 and 1 mM, respectively. The pH of the solutions at a given concentration of ROA does not change significantly as the identity of the ROA is changed. The pH of 3 mM ODA is also ~2.8, and the observed pH for each ROA at 1 mM varies only slightly, between ~3.3 and ~3.7. These pH ranges are in keeping with the previously observed pH for solutions of pyruvic acid at similar concentrations (10 mM ≈ 2.4 and 0.5 mM ≈ 3.5).⁶⁷ This is suggestive that the pK_a of each ROA does not change significantly as alkyl tail length is varied. The effective pK_a of OOA has recently been determined to be 2.78,⁸⁸ which is similar to the well-known effective pK_a of pyruvic acid of 2.49.⁸⁹ The term effective is used to describe these pK_a values because the titration method of determining pK_a necessarily includes contributions from both the keto and the geminal-diol conformers in solution (discussed below), which also each have individual values of pK_a.⁹⁰

For each photolysis, 100 mL solutions were prepared, saving 10 mL as a pre-photolysis control, and photolyzing the remaining 90 mL of solution for 5 h, using a 450 W ozone-free Xe arc lamp (Newport). Solution temperature was controlled by a temperature-stabilized water bath. For the 1 mM solutions of each oxoacid, the water bath was held at 20 °C because of solubility concerns for ODDA. The higher concentrations of OHA, ODA, and OOA were also conducted at 4 °C. No difference was observed in products with changes in the water bath temperature. Unless otherwise stated, each solution was purged with N₂, to displace dissolved O₂. Solutions were purged for the duration of photolysis, beginning 1 h prior to the start of illumination. After photolysis, the solutions were brought to room temperature before any further analyses were conducted.

The absorption maximum of the excitation from the ground state to the S₁, ¹(n, π*), state for each of the oxoacids examined here occurs at λ_{max} ≈ 315 nm. This is a slight blue shift from that of pyruvic acid (λ_{max} ≈ 320 nm),^{28,67} but there is not a significant change in the absorption maximum as a function of changing alkyl tail length for the four oxoacids investigated here (spectra shown in Figure S1).

The spectral output of the unfiltered Xe arc lamp used in these studies extends into the UV to about 220 nm as shown in Figure S1. Therefore, it is likely that, under our experimental conditions, some excitation to the S₂, ¹(π, π*), state also occurs in addition to excitation to the S₁ state. This is unlikely to alter any reaction pathways, as it is known that, upon excitation to higher excited states, such as the S₂ state, systems often rapidly undergo internal conversion to the first excited (S₁) state.^{91,92} This process is expected to occur here, allowing the normal photochemical pathway of intersystem crossing and internal conversion from the S₁ state to the reactive T₁ state to follow. It has been previously observed that the photochemical products generated from the photolysis of pyruvic acid using an unfiltered Xe arc lamp⁶⁷ are in good agreement with those obtained when the Xe lamp is filtered to remove wavelengths λ < 300 nm;²⁸ however, the rate of photolysis is slowed when the Xe lamp is filtered, as would be expected when fewer photons are present. The S₂ state cannot be excited with λ > 300 nm, suggesting the same reactive photochemical pathways are followed when the lamp remains unfiltered, without additional reactive pathways stemming from excitation to the S₂ state. This is consistent with other observations in the literature, which have shown, for example, that the photochemistry of nonanoic acid in aqueous solution is faster but does not result in the formation of different products when an unfiltered Xe arc lamp is used.¹²

Synthesis of Alkyl Oxoacids. The same general procedure was used to synthesize each of 2-oxohexanoic acid, 2-oxodecanoic acid, and 2-oxododecanoic acid. The general synthetic procedure is outlined

Table 1. Select Compiled 2-Oxo-octanoic Acid Photolysis Mass Spectra Data^a

assigned formula [M - H] ⁻	assigned structure	average experimental m/z ^b	theoretical m/z	mass diff. (ppm)	pre-photolysis	post-photolysis
$\text{C}_3\text{H}_3\text{O}_3$	pyruvic acid	87.0092 ± 0.0006	87.0082	10.9	below threshold	weak
$\text{C}_8\text{H}_{13}\text{O}_3$	2-oxooctanoic acid	157.0880 ± 0.0005	157.0865	9.6	strong	strong
$\text{C}_8\text{H}_{13}\text{O}_4$	2,2-DHOA ^c (OOA diol)	173.0826 ± 0.0004	173.0814	7.0	medium	medium
$\text{C}_6\text{H}_9\text{O}_6$	dimethyltartaric acid	177.0411 ± 0.0005	177.0400	6.6	below threshold	weak
$\text{C}_{12}\text{H}_{21}\text{O}_5$	R-DHO acid	245.1400 ± 0.0005	245.1389	4.4	below threshold	medium
$\text{C}_{11}\text{H}_{19}\text{O}_6$	methylhexyltartaric acid	247.1193 ± 0.0005	247.1182	4.6	below threshold	strong
$\text{C}_{13}\text{H}_{21}\text{O}_7$	R-DHO diacid	289.1301 ± 0.001	289.1288	4.7	below threshold	medium
$\text{C}_{17}\text{H}_{31}\text{O}_5$	R,R-DHO acid	315.2181 ± 0.0006	315.2172	3.0	below threshold	strong
$\text{C}_{16}\text{H}_{29}\text{O}_6$	dihexyltartaric acid	317.1973 ± 0.0005	317.1965	2.8	below threshold	strong
$\text{C}_{18}\text{H}_{31}\text{O}_7$	R,R-DHO diacid	359.2071 ± 0.0007	359.2070	0.3	below threshold	medium
$\text{C}_{22}\text{H}_{41}\text{O}_5$	R,R,R-DHO acid	385.2958 ± 0.0003	385.2954	0.8	below threshold	medium
$\text{C}_{23}\text{H}_{41}\text{O}_7$	R,R,R-DHO diacid	429.2855 ± 0.0008	429.2860	-1.2	below threshold	weak

^aChemical formulas are assigned as the ionized [M - H]⁻ species; structures are assigned as the neutral species. ^bThe experimental m/z is the observed average across experiments, and the uncertainty given is the 95% confidence interval. ^c2,2-DHOA = 2,2-dihydroxyoctanoic acid, the gem-diol form of OOA.

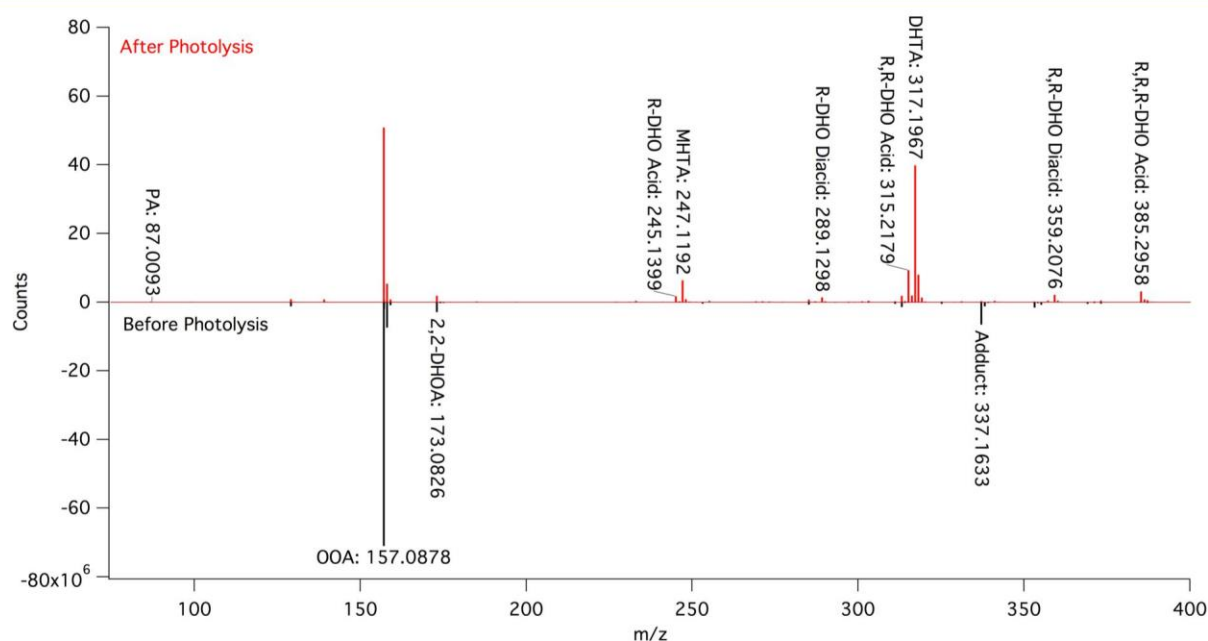


Figure 1. Representative MS of 3 mM OOA pre (black, counts multiplied by -1 for ease of presentation) and post (red) 5 h of photolysis in N₂; high molecular weight products are not observed.





















below. Detailed information and characterization of each synthesized oxoacid are given in the [Supporting Information](#), along with ¹H and ¹³C NMR spectra (Figures S2-4). A solution of the Grignard reagent, prepared from the appropriate 1-bromoalkane and the suspension of magnesium in THF, was added dropwise under N₂ atmosphere to a cold (-78 °C) solution of diethyloxalate in THF. After the addition was complete, the reaction mixture was stirred at -78 °C for at least an additional hour. The reaction was quenched with 2 N HCl, and the aqueous layer was extracted with either ether or hexanes. The combined organic layers were washed with saturated NaCl, dried over MgSO₄, and evaporated. The crude product was then purified either by distillation under reduced pressure to give a colorless oil (OHA) or by recrystallization in hexanes to give a white solid (ODA and ODDA).

Product Analysis. Detailed information and instrument parameters for the analytical techniques used to characterize the photolysis solutions (dynamic light scattering, UV-vis and NMR spectroscopy, and high-resolution negative mode electrospray ionization mass spectrometry) are given in the [Supporting Information](#). In the ESI⁻ MS, both [M - H]⁻ and singly charged adduct ions are observed for the analytes of interest under the ionization conditions used here. The

observed noncovalent adduct ions are formed from the coordination of two or more deprotonated organic species with a metal ion and a net charge of -1. We observe, primarily in the pre-photolysis controls, adduct ions consisting of multiple deprotonated oxoacid molecules coordinated with a positive counterion, usually Na⁺ or Ca²⁺. All photolyses were conducted in 18.2 MΩ water without the addition of salt to minimize the presence of such adduct ions, and any metal ions are assumed to be present only in trace quantities in solution.

The ESI⁻ MS analysis used here was not designed to be absolutely quantitative. As expected for solutions containing mixtures of analytes, the observed intensities of [M - H]⁻ ions vary considerably due to variations in ionization efficiency as well as differences in concentration of species. To avoid incorrect ion assignments to noise peaks, a conservative intensity threshold of 10⁴ counts was imposed for analyte identifications; the average noise threshold across runs is about 1000 counts. To allow for qualitative comparisons, categories of relative signal intensity were defined as follows: for given monoisotopic ions, those with intensities greater than 10⁶ counts are "strong", those with intensities greater than 10⁵ counts are "medium", and those with intensities greater than 10⁴ counts are "weak". These intensity categories are used only for relative comparisons because

Table 2. Summary of Key MS Data for OHA, ODA, and ODDA^a

identity	2-oxohexanoic acid, R = (CH ₂) ₂ CH ₃		2-oxodecanoic acid, R = (CH ₂) ₆ CH ₃		2-oxododecanoic acid, R = (CH ₂) ₈ CH ₃		pre-hv ^c	post-hv ^c
	[M - H] ⁻ 	avg exp m/z ^b (ppm)	[M - H] ⁻ 	avg exp m/z ^b (ppm)	[M - H] ⁻ 	avg exp m/z ^b (ppm)		
ROA		129.0550(-1.5)		185.1186(4.5)		213.1502(5.2)	S	S
R-DHO acid		217.1077(0.3)		273.1708(1.9)		301.2025(3.2)	B.T.	M
R,M-TA ^d		219.0868(-0.5)		275.1500(1.8)		303.1820(4.0)	B.T.	M
R,R-DHO acid		259.1546(-1.5)		371.2805(1.9)		427.3450(6.1)	B.T.	M
R,R-TA ^e		261.1339(0.0)		373.2595(1.2)		429.3215(-0.3)	B.T.	S
R,R,R-DHO acid		301.2015(0.6)		469.3890(-0.7)	B.T.		B.T.	M

^aChemical formulas are assigned as the ionized [M - H]⁻ species; structures are assigned as the neutral species. ^bThe experimental m/z is the average observed mass across experiments. Values in parentheses are the averaged mass differences from the theoretical m/z given in ppm. ^cRelative intensities of the observed MS species are given as S = strong, M = medium, B.T. = below threshold. ^dR,M-TA = R,methyl-tartaric acid. ^eR,R-TA = R,R-tartaric acid.

they do not necessarily directly correlate to absolute analyte concentrations.

RESULTS AND DISCUSSION

Here, we report on the generation of surface-active oligomers from the aqueous photochemistry of a series of four α -keto acids with differing alkyl tail lengths (2-oxohexanoic acid (OHA), 2-oxooctanoic acid (OOA), 2-oxodecanoic acid (ODA), and 2-oxododecanoic acid (ODDA) shown in [Chart 1](#)). The photochemical mechanisms governing this chemistry follow those that have been previously reported in the literature,^{52,93-95} primarily from detailed studies of the aqueous photolysis of pyruvic acid.^{28,62,64,65,67,96,97} Here, we perform a detailed high-resolution negative mode electrospray ionization mass spectrometry (ESI⁻ MS) analysis, supported by NMR studies, to show that this chemistry is robust and broadly transferable to a whole class of molecules with the same reactive functionality and generates multi-tailed lipids.

The aqueous photolysis of each oxoacid we study here follows the same general mechanism, regardless of the alkyl tail length, detailed descriptions of which can be found in previous work on pyruvic acid.^{28,64,67} For clarity, here we will describe briefly the mechanistic pathways of this chemistry for the general case of an oxoacid with an arbitrary alkyl tail, R, abbreviated as ROA. The photochemistry holds for each of the specific alkyl tails examined (R = (CH₂)₂CH₃, (CH₂)₄CH₃, (CH₂)₆CH₃, and (CH₂)₈CH₃). Similarities and differences between the known photochemical behavior of pyruvic acid (R = H) will be discussed when relevant.

The solubility of the molecules investigated decreases as a function of chain length, so to facilitate comparison across alkyl tail lengths, photolyses for each oxoacid were conducted at concentrations of ~1 mM and at 20 °C. These experimental conditions approached the solubility limit of ODDA. Photolyses of 6 and 3 mM OOA and 3 mM ODA were also conducted at 4 °C. There were no observable differences in the products generated during photolysis when the water bath temperature was changed from 4 to 20 °C for OOA and ODA.

Despite the low concentrations required, photochemical products were still readily observed for each oxoacid. Averaged MS results for OOA are given in [Table 1](#) with representative mass spectra for both the pre- and the post-photolysis solutions of OOA given in [Figure 1](#). A summary of the MS results for the other alkyl oxoacids, OHA, ODA, and ODDA, is given in [Table 2](#). Detailed MS results for each oxoacid are also given in [Figures S5-7](#) and [Tables S1-4](#).

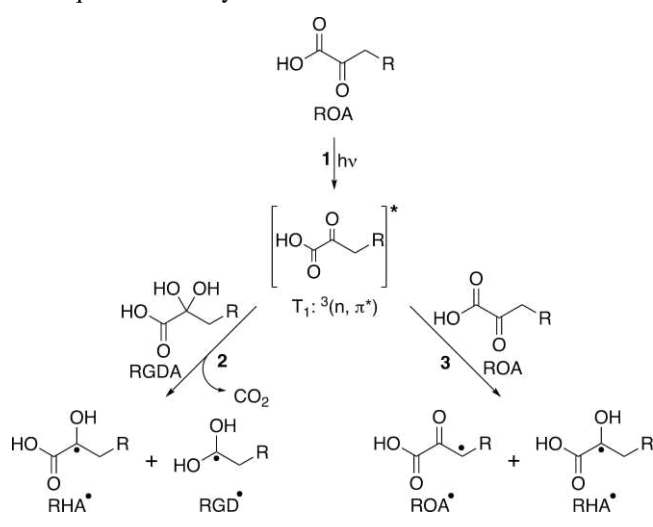
In aqueous solution, the ketone group of ROA can be hydrated to the geminal diol form of the acid, R,gem-diol-

alkanoic acid (RGDA).^{28,64,67} These 2,2-dihydroxyalkanoic acids, unlike the keto conformer, do not absorb light within the solar spectrum. Unlike many α -dicarbonyl species, which are almost completely hydrated in aqueous solution, oxoacids retain a significant amount of ketonic functionality.^{90,98,99} It has been shown for pyruvic acid that the extent of hydration is concentration-, pH-, and temperature-dependent,^{67,90,99-101} with percentages of diol conformer ranging from ~65% at 100 mM to ~50% at 10 mM concentrations.^{28,63,67} The longer-tailed oxoacid species under study here retain significantly more ketonic functionality in aqueous solution than pyruvic acid. The 6 mM OOA at ambient temperature exists as roughly 80% keto and 20% diol in solution as characterized by NMR ([Figure S8](#)). Both conformers are also observed in the MS data ([Figure 1](#) and [Table 1](#)). The ratio of keto to diol conformers does not appear to change as a function of tail length for any of the longer-tailed species we investigate here. For example, ODA, which has two more carbons than OOA in its alkyl chain, also exists as an approximately 80% keto conformer in solution under our reaction conditions ([Figure S9](#)).

Additionally, even under our acidic reaction conditions, because the effective pK_a of alkyl oxoacids is about ~2.6,^{88,89} a significant percentage of ROA are deprotonated in solution, with preferential deprotonation of the photoactive, keto conformer.⁹⁰ This reduces the number of photoactive protonated species available for excitation, and at higher pH the rate of photolysis for pyruvic acid has been observed to slow.⁶⁵ However, under our acidic reaction conditions, the photochemistry still readily proceeds.

In aqueous solution, photolysis begins when the oxoacid, ROA, is excited by a UV photon from the ground state to the S₁, ¹(n, π^*), state ($\lambda_{\text{max}} \approx 315$ nm), which is followed by intersystem crossing and internal conversion to the T₁, ³(n, π^*), state (reaction 1 of [Scheme 1](#)). ROA in the excited T₁ state then forms radical species by abstracting a hydrogen from another oxoacid, which can occur via two different pathways ([Scheme 1](#)),⁶⁷ depending on the site of hydrogen abstraction. In the first (reaction 2 of [Scheme 1](#)), hydrogen abstraction occurs at the carboxyl group of either ROA or its geminal diol form (RGDA) and is followed by decarboxylation to form two radical species, one with hydroxy-acid functionality (denoted RHA^{*}) and one with geminal diol functionality (denoted RGD^{*}). For pyruvic acid, abstraction from the diol form is favored energetically, but it has been shown that abstraction from the keto conformer can also occur.⁶⁴ Even with the lower

Scheme 1. Formation Pathways of Radical Species during the Aqueous Photolysis of Oxoacids¹⁰²



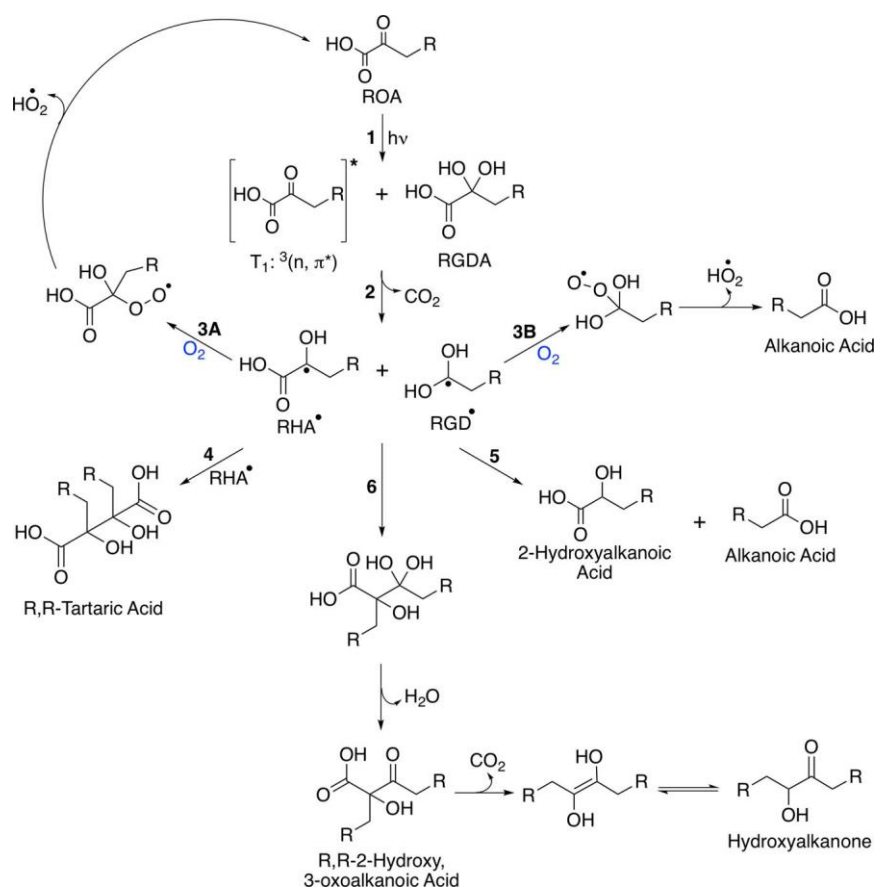
amounts of diol observed for ROA as compared to pyruvic acid, it is clear from the products observed by ESI[−] MS that hydrogen abstraction at the carboxyl group readily occurs for all of the oxoacids under consideration here and is likely the dominant site of abstraction.

In the second possible pathway (reaction 3 of Scheme 1), the excited ROA in the T_1 state abstracts a hydrogen from the alkyl tail of another, ground-state ROA. Calculations have shown that hydrogen abstraction from the methyl group of pyruvic

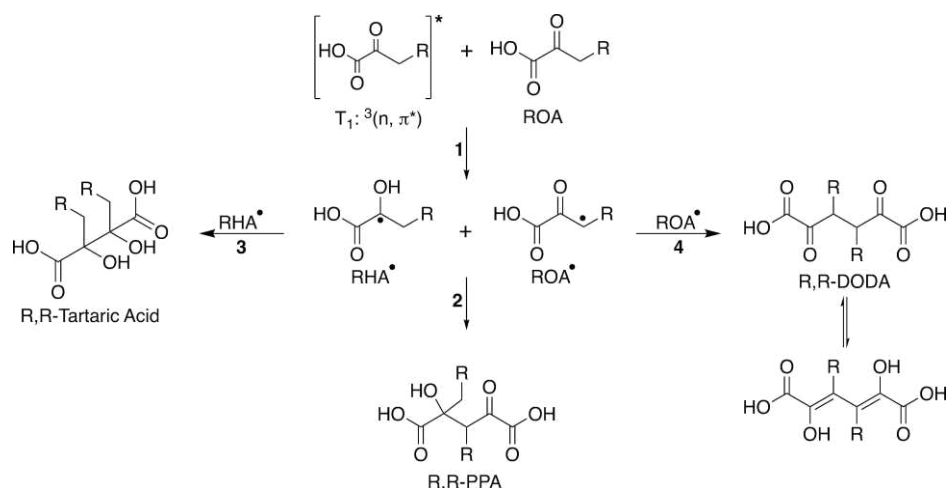
acid is likely to be competitive with hydrogen abstraction from the carboxyl group.⁶⁷ This competitiveness of this pathway is also likely increased in dilute solutions where pH is slightly higher because the methyl group becomes the only site available for abstraction when the keto form of pyruvic acid is deprotonated.⁶⁷ It is reasonable, then, to assume that abstraction from the alkyl tail for ROA is likewise energetically competitive, occurring to some extent during photolysis, yielding both a radical that retains oxoacid functionality (ROA•) and RHA•. We have drawn, throughout our discussion, the hydrogen abstraction to form ROA• as occurring at the β -CH₂ group. While abstraction from this site may be favored, it can, in principle, occur anywhere along the alkyl chain.¹⁰³ Products that are generated from subsequent reactions of ROA• are observed in the MS of post-photolysis solutions, but ESI[−] MS alone cannot differentiate where along the alkyl chain hydrogen abstraction has occurred. It is likely that the observation of a given chemical formula in the MS data corresponds to a mixture of constitutional isomers.

The three radical species (RHA•, RGD•, and ROA•) generated by these two hydrogen abstraction processes can recombine following a variety of pathways, explaining the majority of the observed photoproducts for each of the oxoacids under study here (Tables 1 and 2, with detailed MS results for each ROA in Tables S1–4). The products observed from further reactions of the radical pair, RHA• and RGD•, generated by hydrogen abstraction from the carboxyl group, are outlined in Scheme 2. Tartaric acid derivatives with two alkyl chains (R,R-tartaric acid), are formed from the recombination

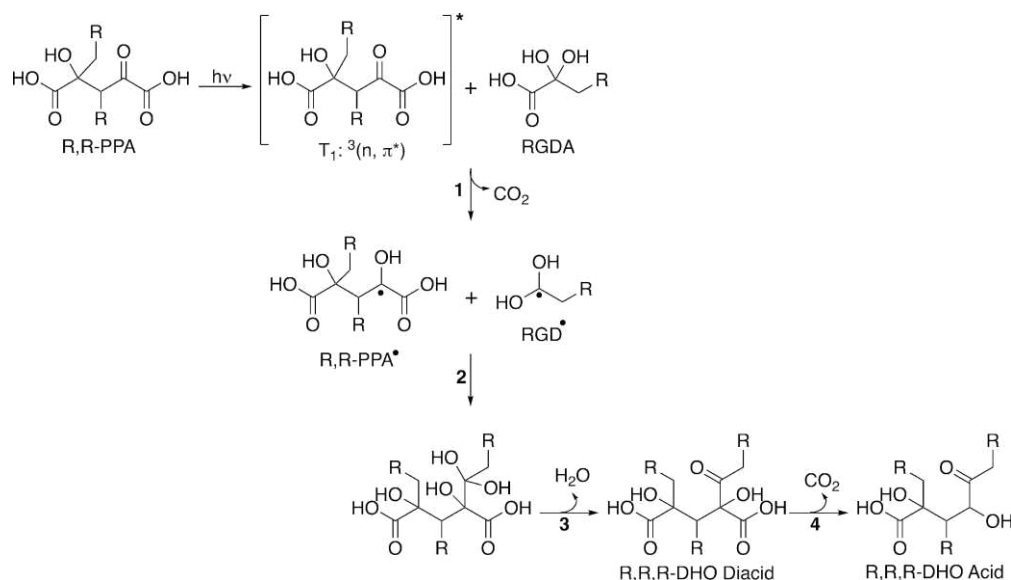
Scheme 2. General Photochemical Pathways of Alkyl Oxoacids Following Carboxyl Hydrogen Abstraction



Scheme 3. Potential Recombination Pathways for Alkyl Oxoacids Following Alkyl Hydrogen Abstraction To Form ROA[•] ¹⁰²



Scheme 4. Photochemistry of R,R-PPA (Here Shown As Formed from a β -CH₂ ROA[•]) To Generate Trimer Species of ROA ¹⁰²



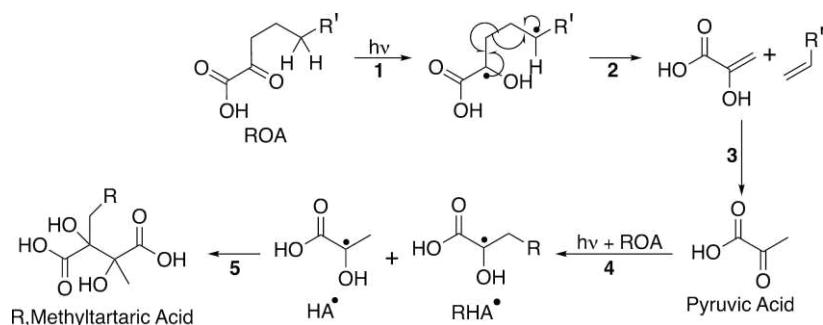
of two RHA[•] radicals, as shown by reaction 4 of [Scheme 2](#). R,R-Tartaric acid (e.g., dihexyltartaric acid for OOA) appears to be one of the major photochemical products formed during photolysis for each of the oxoacids under study here. It is observed as the photoproduct with the highest intensity in the MS data in each of the post-photolysis solutions analyzed, regardless of whether the photolysis was conducted in air or under N₂. However, this is only a relative comparison as our ESI[−] MS analysis was not designed to be absolutely quantitative. The “R’s” used in the names of product species throughout our discussion simply denote the presence of an alkyl chain; the “R’s” do not represent an attempt at assigning the stereochemistry of these molecules, even though these tartaric acid derivatives do contain chiral centers (the implications of which are discussed further below).

Further reactions stemming from the recombination of RHA[•] and ROA[•] generated by hydrogen abstraction from the alkyl tail of ROA account for several of the other main photoproducts observed by MS. As shown in reaction 2 of [Scheme 3](#), the recombination of RHA[•] and ROA[•] forms a derivative of parapyruvic acid with two alkyl chains, R,R-parapyruvic acid (R,R-PPA), which is observed in the MS for

each of the ROAs under study here ([Tables S1–4](#)). The reactions in [Scheme 3](#) have been drawn showing hydrogen abstraction occurring at the β -CH₂ group, but it is possible for the hydrogen abstraction that generates ROA[•] to occur anywhere along the alkyl tail.

In addition to the R,R-PPA and R,R-tartaric acid species, we have tentatively detected dioxoacid species, R,R-dioxodiacid (R,R-DODA), as photoproducts for most of the ROA under study. Generated from the recombination of two ROA[•] radicals, as shown in reaction 4 of [Scheme 3](#), R,R-DODA likely exists in equilibrium with the enol in aqueous solution. In the post-photolysis solutions for OHA, ODA, and ODDA, we observe ions corresponding to the chemical formulas of R,R-DODA in the MS ([Tables S2–4](#)). However, because the intensities of the observed ions are at the cutoff threshold for detection for all three oxoacids, these assignments are tentative. Nevertheless, these tentative detections help answer questions about the photochemical mechanism underlying the production of R,R-PPA.⁶⁷ The recombination of ROA[•] and RHA[•] that generates R,R-PPA cannot occur immediately after the two radicals are generated by hydrogen abstraction along the alkyl tail (reaction 1 of [Scheme 3](#)) because the radical pair generated

Scheme 5. General Norrish Type II Reaction Scheme for ROA



has an overall net triplet character, preventing intracage geminate recombination. Instead, before the radicals can react further, they must either undergo intersystem crossing back to the singlet state or undergo cage escape, either of which is possible. If intersystem crossing back to the singlet state is favored, then only R,R-PPA species should be detected; however, if the radicals undergo cage escape, then products from each of the potential recombination processes for the RHA[•] and ROA[•] radicals should also be observed. As shown in reaction 3 of Scheme 3, the recombination of RHA[•] radicals formed from this channel can also contribute to the formation of R,R-tartaric acid, while the recombination of ROA[•] radicals leads to R,R-DODA as mentioned above. In the previous study of pyruvic acid that initially proposed this mechanism, the dioxoacid, 2,5-dioxohexanedioic acid, was not observed in the MS,⁶⁷ possibly because of its own ability to react photochemically. This means that there was no way of differentiating between cage escape and intersystem crossing back to the singlet state, which would only generate parapyruvic acid as a product.⁶⁷ Here, the presence of R,R-DODA species suggests that cage escape is the favored route by which the generated radical pair can recombine, rather than intersystem crossing back to the singlet state.

Regardless of the path by which they are formed, the R,R-PPA species created by the recombination of RHA[•] and ROA[•] are themselves photoactive. They are also α -keto acids and can, therefore, undergo the same photochemistry as other alkyl oxoacids, as shown in Scheme 4. Photoexcited R,R-PPA can then encounter another ROA, or the corresponding RGDA in solution, which then decarboxylates, following the pathway outlined in reaction 2 of Scheme 2, generating both a RGD[•] radical and a R,R-PPA radical (R,R-PPA[•]), as shown in reaction 1 of Scheme 4. These two radicals can then combine, following reactions 2 and 3 of Scheme 4, generating a dihydroxyoxo-dialkanoic acid with three alkyl chains (R,R,R-DHO diacid) and, following decarboxylation, a dihydroxyoxoalkanoic acid (R,R,R-DHO acid). The R,R,R-DHO acid is observed in the MS for each of the ROA except for ODDA (Tables 1 and 2). The intermediate, R,R,R-DHO diacid, is, however, observed for ODDA (Table S4), as it is for ODA and OOA. For OHA, the R,R,R-DHO diacid is observed readily at 6 mM, but it is below the threshold for detection in the 1 mM solutions.

In addition to the photochemical pathways discussed above where organic radicals are generated from bimolecular interactions, there is also a unimolecular photochemical reaction pathway.⁵² For the four ROA species investigated here, photoexcitation can lead to an intramolecular Norrish Type II reaction as shown in Scheme 5. This is in contrast to pyruvic acid, which does not have an alkyl chain with the γ -

carbon that is necessary for this chemistry to proceed. There has been some debate in the literature as to whether the Norrish Type II reaction happens from the singlet or the triplet

state, with Davidson et al. presenting evidence for its

occurrence on the singlet state.⁹⁴ Regardless of the manifold on which it occurs, the Norrish Type II reaction generates a biradical on the oxoacid (reaction 1, Scheme 5) that then leads to homolytic bond cleavage (reaction 2, Scheme 5).

This additional pathway adds considerably to the complexity of the photoproducts observed for longer-tailed alkyl oxoacids as compared to pyruvic acid. The 2-hydroxy-3-propenoic acid generated by bond cleavage of the ROA in reaction 2 of Scheme 5 can rearrange to form pyruvic acid, as shown in reaction 3 of Scheme 5. This photochemically synthesized pyruvic acid can, of course, undergo all of its normal aqueous photochemistry,^{28,64,67} including generating dimethyltartaric acid and 2,4-dihydroxy-2-methyl-5-oxohexanoic acid (DMOHA). Both of these species are observed in post-photolysis solutions for each ROA. The intensities of these species in the MS are near the threshold for detection, as would be expected given the probability of two minor species encountering each other in solution.

It is far more likely that the photochemically generated pyruvic acid would encounter an ROA molecule, leading to a cross-reaction between the two species. The most direct reaction involves the encounter of two radicals with hydroxy-acid functionality HA[•] from pyruvic acid and RHA[•] from ROA. The recombination of these two species forms a tartaric acid derivative with one methyl and one alkyl chain, R,methyl-tartaric acid (reaction 5 of Scheme 5). The R,methyl-tartaric acid species generated by this process was also observed clearly by MS as one of the main photoproducts for each of the four oxoacids.

As the radical species under study here are promiscuous and because of the formation of pyruvic acid from ROA via the Norrish Type II reaction, the photolysis of ROA leads to complex mixtures of products. Intermediate species, such as R,R-PPA and pyruvic acid, that can go on themselves to do further photochemistry, widely expand the photoproducts that can be formed. The formation of pyruvic acid in solution with ROA means that not only can R,R-PPA be formed from two ROA[•] radicals recombining, but R-PPA from the recombination of one ROA[•] and the pyruvic OA[•] and even parapyruvic acid itself from the recombination of two OA[•] can be formed. R-PPA species are observed for each of the oxoacids, although not for 1 mM OHA. The presence of parapyruvic acid is not observed by MS, but its concentration would be expected to be low due to the relatively low statistical probability of its formation.

Scheme 6. Select Possible Reaction Pathways for ROA[•] Derived from Hydrogen Abstraction from the β-CH₂ of OOA To Form R,R,R-DHO Acid Species, Where R = (CH₂)₄CH₃¹⁰²

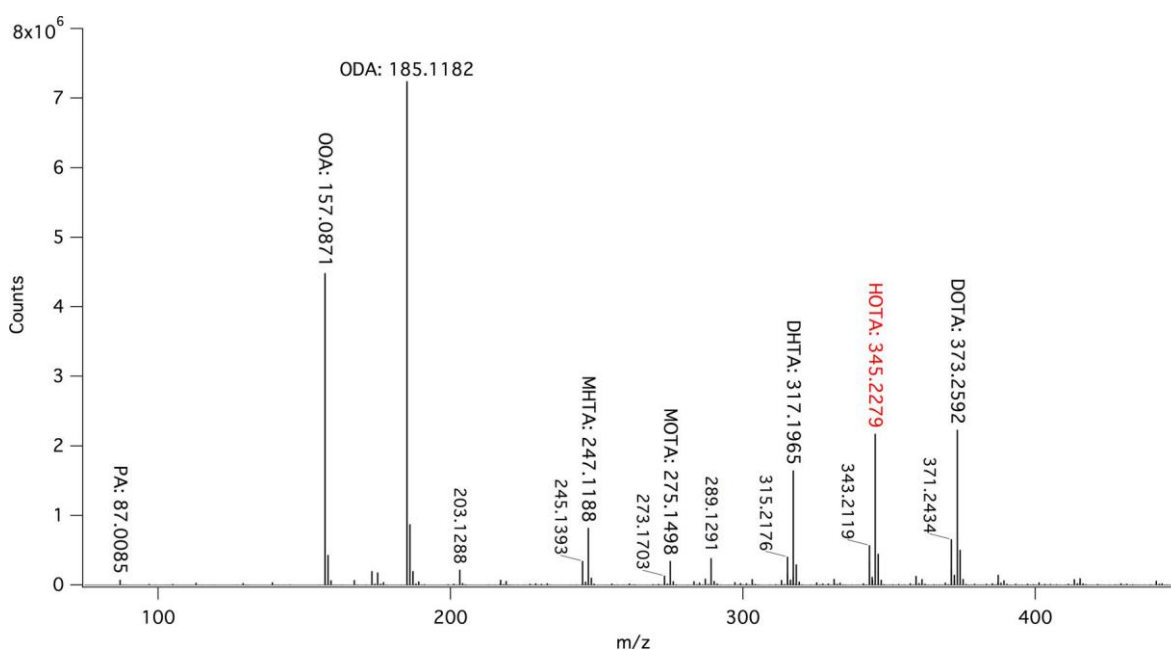
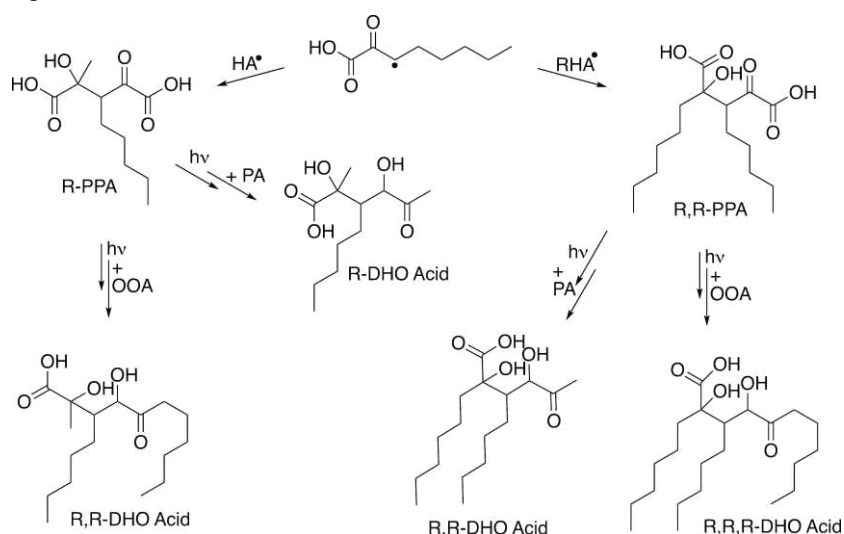


Figure 2. Representative MS of 3 mM OOA and 3 mM ODA after 5 h of photolysis under N₂.

R,R-PPA, R-PPA, and parapyruvic acid are oligomeric intermediate species that can go on to interact with either another ROA or pyruvic acid molecule in solution, following the reactions outlined in Scheme 4. This leads to the possible formation of several DHO diacid and DHO acid species, a few of which are shown in Scheme 6 for OOA. Even assuming the only site of hydrogen abstraction on the alkyl tail of ROA is the β-CH₂ group, there are a number of constitutional isomers possible for the R-DHO acid and R,R-DHO acids. Scheme 6 shows two such R,R-DHO acids, one generated by the reaction of R,R-PPA with a pyruvic acid molecule and one generated by the reaction of one of the potential isomers of R-PPA with OOA. Clearly there are other possible reactions that generate species with the same chemical formula and reactive functionality but different tail positions. Considering the potential for hydrogen abstraction from multiple sites along the alkyl tail considerably expands the pool of potential

constitutional isomers generated by this chemistry as well. R,R-DHO acid and R-DHO acids are observed in the MS of the post-photolysis solutions for each of the ROA studied here, as are the corresponding diacid intermediates, with each observable peak likely corresponding to a mixture of constitutional isomers.

Pathways that generate reactive intermediate species, such as the formation of R,R-PPA and pyruvic acid, ensure that even an initial solution of a single ROA develops into a complex, interconnected network of reactions that generate a rich mixture of oligomeric photoproducts upon photolysis. The radicals generated by the photolysis of oxoacids are capable of interacting not just with another identical oxoacid molecule but also with other radical species present in solution. Here, we show that the ability for cross-reactions carries through to the reaction between two different ROAs in solution, photolyzing a mixed solution of OOA and ODA. A representative post-

Table 3. New Photoproducts from the Mixed Photolysis of OOA and ODA^a

assigned formula [M - H] ⁻	assigned structure	avg exp m/z ^b	mass diff. (ppm)	pre-photolysis	post-photolysis
$\begin{smallmatrix} \text{C}_{18}\text{H}_{31}\text{O}_6 \\ \text{C}_{19}\text{H}_{35}\text{O}_5 \end{smallmatrix}$	R,R'-PPA	343.2113	-2.5	medium	medium
$\begin{smallmatrix} \text{C}_{18}\text{H}_{33}\text{O}_6 \\ \text{C}_{20}\text{H}_{35}\text{O}_7 \end{smallmatrix}$	R,R'-DHO acid	343.2490	1.5	below threshold	medium
$\begin{smallmatrix} \text{C}_{24}\text{H}_{45}\text{O}_5 \\ \text{C}_{26}\text{H}_{49}\text{O}_5 \end{smallmatrix}$	hexyloctyltartaric acid	345.2280	0.75	below threshold	strong
$\begin{smallmatrix} \text{C}_{24}\text{H}_{45}\text{O}_5 \\ \text{C}_{25}\text{H}_{45}\text{O}_7 \end{smallmatrix}$	R,R'-DHO diacid	387.2380	-0.80	below threshold	medium
$\begin{smallmatrix} \text{C}_{24}\text{H}_{45}\text{O}_5 \\ \text{C}_{25}\text{H}_{45}\text{O}_7 \end{smallmatrix}$	R,R,R'-DHO acid	413.2370	0.65	below threshold	medium
$\begin{smallmatrix} \text{C}_{24}\text{H}_{45}\text{O}_5 \\ \text{C}_{25}\text{H}_{45}\text{O}_7 \end{smallmatrix}$	R,R',R'-DHO acid	441.3575	-1.2	below threshold	medium
$\begin{smallmatrix} \text{C}_{25}\text{H}_{45}\text{O}_7 \\ \text{C}_{27}\text{H}_{49}\text{O}_7 \end{smallmatrix}$	R,R,R'-DHO diacid	457.3175	2.0	below threshold	weak
$\begin{smallmatrix} \text{C}_{25}\text{H}_{45}\text{O}_7 \\ \text{C}_{27}\text{H}_{49}\text{O}_7 \end{smallmatrix}$	R,R',R'-DHO diacid	485.3480	0.27	below threshold	weak

^aChemical formulas are assigned as the ionized [M - H]⁻ species; structures are assigned as the neutral species. Here, R = (CH₂)₄CH₃ from OOA and R' = (CH₂)₆CH₃ from ODA. ^bThe experimental m/z is the average observed mass across experiments.

photolysis mass spectrum is shown in Figure 2, with key results in Table 3 (a representative pre-photolysis spectrum is given in Figure S10).

As shown in Scheme 5, when both OOA and ODA are in solution, the R,R-tartaric acid species generated are not only the corresponding dihexyltartaric acid (DHTA) and dioctyltartaric acid (DOTA), but also the tartaric acid species with differing tail lengths, hexyloctyltartaric acid (HOTA). As shown in Figure 2, when equal amounts of OOA and ODA are present in solution, the amount of HOTA generated is comparable to both DOTA and DHTA, suggesting that there is no great preference for like radicals to recombine with each other. This observation is unsurprising because to form the R,R-tartaric acid, RHA[•] must undergo cage escape, and therefore is no particular preference for either the partner in the solvent cage or the radicals encountered following cage escape.

In addition to the mixed R,R'-tartaric acid, HOTA, the mixed DHO acid and DHO diacid products are also observed, as shown in Table 3. The R,R'-PPA species is formed from the recombination of either a ROA[•] and a R'HA[•] or a R'OA[•] and a RHA[•]. Any ROA[•] radical may, in principle, have the radical anywhere along the alkyl tail, as well, which further expands the number of possible isomers. Each of R,R-PPA, R',R'-PPA, R-PPA, R'-PPA, parapyruvic acid, and this new species R,R'-PPA can go on to react with either OOA, ODA, or pyruvic acid in solution. Of the many possible recombination products, the mixed trimer species, R,R',R'-DHO acid, R,R,R'-DHO acid, and the R,R'-DHO acid, are newly observed photoproducts, along with the corresponding DHO diacid intermediate species.

Clearly, the introduction of even one other starting species greatly adds to the already complex mixture of photoproducts that may be generated from alkyl oxoacids. However, it is worth noting that, while there are many possible oligomeric photoproducts that may be generated, each with several potential constitutional isomers, the photochemistry under study here can be explained using variants on well-understood mechanistic motifs,^{28,52,64,67} identifying a clear majority of the observed photochemical products, even for the mixed ROA solutions. Indeed, even the generation of R,R-DHO acid from the further reactions of R,R-PPA is, essentially, an equivalent reaction pathway to that which forms hydroxyalkanone (acetoin for pyruvic acid⁶⁴) from the decarboxylation of the β -keto acid, R,R-2-hydroxy, 3-oxoalkanoic acid, which is generated from the recombination of RHA[•] and RGD[•], as shown in reaction 6 of Scheme 2.⁶⁷ The R,R-2-hydroxy, 3-oxoalkanoic acids are observed by MS for each ROA (Tables S1-4), and for OOA the hydroxyalkanone is also observed as a minor photoproduct. However, this species is not observed above our detection threshold for any of the other ROA.

Simple fatty acid species (alkanoic acid) are also generated as a minor product from the photolysis of ROA, following reaction 5 of Scheme 2. The alkanolic acid (e.g., heptanoic acid for OOA) is detected both before and after photolysis. It is likely that fatty acids are a common contaminant of the initial ROA starting material, just as acetic acid is a known contaminant of pyruvic acid. Interestingly, the corresponding 2-hydroxyalkanoic acid is not observed by MS for the ROA examined here. It has been previously shown that simple carboxylic acids do not have a strong intensity in the ESI⁻ MS under the experimental conditions used here,⁶⁷ and, given the presence of many other more surface-active photoproducts, the intensity of the MS signal is not quantitatively reflective of their concentration in solution. However, this may also indicate that the branching ratio of products observed for the longer-tailed, alkyl ROA differs somewhat from pyruvic acid. While both acetic acid and lactic acid generated from pyruvic acid following reaction 5 of Scheme 2 are minor photoproducts under oxygen-limited conditions, they are readily observed by NMR,^{28,64,67} and lactic acid has been observed by MS as well.⁶⁷

Small changes in product branching ratios between pyruvic acid and the longer-tailed ROA, such as OOA, would not be surprising. It also appears that OOA has a slower rate of reaction than pyruvic acid. Quantifying the amount of OOA consumed during photolysis is more difficult than for pyruvic acid because of the additional signal in the NMR due to the hydrogens on the alkyl chains, but we estimate that for the 3 mM OOA solutions approximately 30% of the OOA is consumed after 5 h of photolysis. This is a smaller yield than for pyruvic acid (~90% consumed) under similar reaction conditions.⁶⁷ It is possible that we are underestimating the consumption of OOA, as the signal from some H atoms may be lost through the production of volatile species that partition to the gas phase, the formation of water, or due to the large aggregates we observe, which will have low NMR response. The aggregates formed by OOA photolysis are discussed further below.

There are several likely contributing factors for this apparent decrease in reactivity for the longer-tailed oxoacid. Hydrogen abstraction is favored energetically from the diol form of the oxoacid rather than the keto form; therefore, the chemistry might be less favorable because the ratio of diol to keto shifts for the longer-tailed species. For solubility reasons, we used lower concentrations of OOA than have been used for pyruvic acid (~3–6 mM OOA vs 10 mM PA).⁶⁷ Because the chemistry used to generate the oligomeric products relies on radical species encountering each other, the kinetics of reaction likely decrease for lower concentrations of oxoacid.

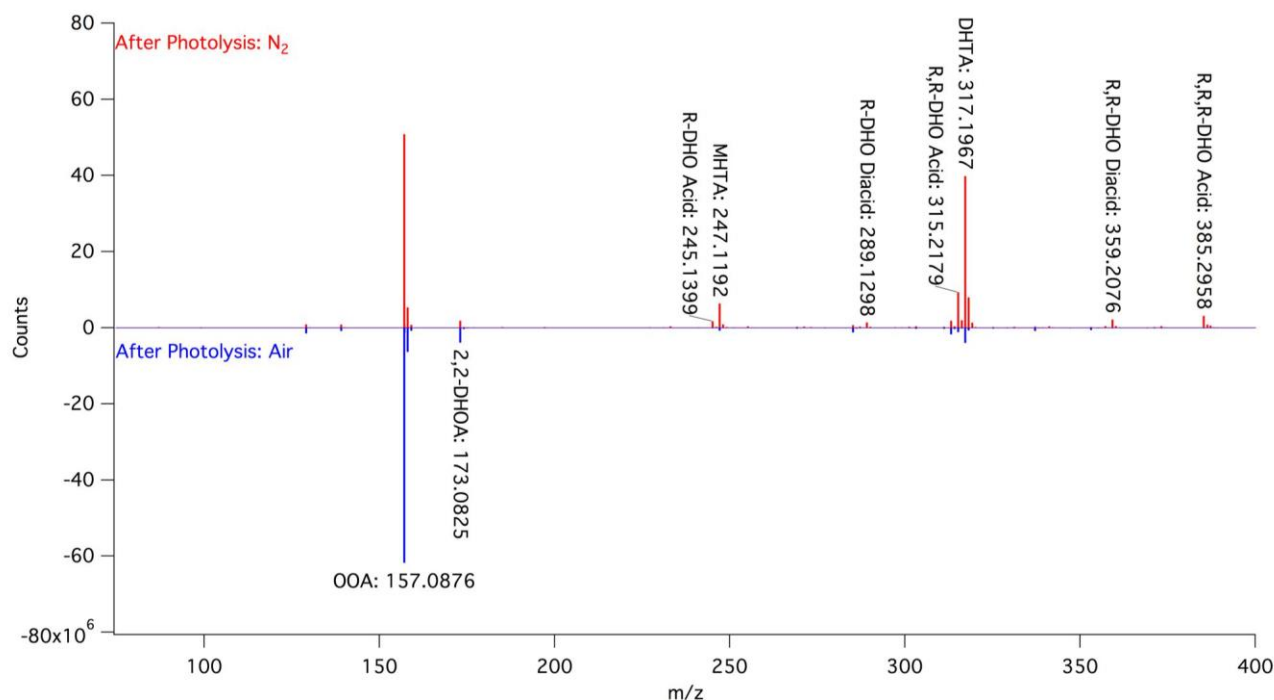


Figure 3. Representative MS of 3 mM OOA after 5 h of photolysis under N_2 (red) and open to air (blue, counts multiplied by -1 for ease of presentation).

While the product yields and the exact branching ratios may differ slightly between pyruvic acid and the ROA studied here, the chemistry retains its sensitivity to environmental conditions even when longer alkyl chains are added to the oxoacids. The ESI^- MS experiments used here were not designed to be quantitative, but these results can be used to infer qualitative differences in product yields when comparing very similar samples, especially if the effect is large. As shown in Figure 3, the difference between the post-photolysis samples that were irradiated in air versus in nitrogen is stark. While the oligomeric dihexyltartaric acid is the major observed product under both conditions, considerably more oligomeric products are formed in a nitrogen environment. Interestingly, while this effect is also seen in the NMR, the overall decrease in OOA concentration is only modestly increased under a nitrogen atmosphere (Figure S11), shifting from approximately 20% consumption in air to 30% in nitrogen following 5 h of photolysis. As mentioned above, this relatively small shift could be due to the loss of signal when the generated products are tied up into larger aggregates. Additionally, because the products generated by photolysis are oligomers of OOA, even a relatively modest change in overall consumption can have a large effect on the formation and yield of photoproducts. For example, there is a noticeable decrease in the relative amounts of the oligomeric photoproducts that are formed from the further reactions of species generated by photolysis, such as methylhexyltartaric acid and the DHO acid species. This result suggests that those processes that require two photochemical steps are less favored in the presence of oxygen, which can act as a radical quencher.

We have observed here, for the first time, that environmental conditions such as the concentration of oxygen in the photolysis reactor affect the longer-tailed oxoacids in the same manner as has been demonstrated for pyruvic acid.²⁸ The increased yield of such oligomers in the absence of oxygen is to be expected, given both that oxygen is known to quench triplet state chemistry and that oxoacids may be regenerated through

reactions with oxygen (reaction 3A in Scheme 2). However, it is worth noting that, while the formation of oligomeric products is reduced when oxygen is present in solution, oligomers are still formed and are the major observable product. This is consistent with previous studies on pyruvic acid that show that oligomers are formed in the presence of oxygen,^{28,69} including under conditions that closely replicate the modern atmosphere.⁶⁸ Nevertheless, the ability to shift the reaction branching ratios by shifting environmental conditions has significant implications, especially for longer, lipid-like oxoacids.

Anoxic conditions favor the formation of more complex oligomeric species, many of which have two or three alkyl chains. This dependence is intriguing because the prebiotic atmosphere, unlike that of today, contained very little O_2 and ozone, allowing more UV light to reach the Earth's surface.^{4,104} The absence of oxygen in the prebiotic atmosphere would render the common, modern photo-oxidation reactions with hydroxyl radical negligible and makes it likely that direct photochemistry of carbonyl-containing compounds would be a more significant process on the ancient Earth than it is today. This points to the potential of such chemistry to generate more complex, double- and triple-tailed amphiphiles under prebiotically relevant conditions. This chemistry is among one of the only processes by which multi-tailed lipids from single-tailed precursors can be formed simply and in relatively high yields under prebiotically plausible conditions and using prebiotically plausible precursors.^{4,52}

The generation of a large library of photoproducts, including that of mixed oligomeric species from two different ROA, shows the specificity of the photochemistry governing the formation of the radicals from oxoacids, while also demonstrating their ability to react promiscuously with other species in solution. The reactivity of mixtures and the ways in which such mixtures produce molecular complexity is inherently more applicable to environmental chemistry whether on the modern or ancient Earth than single molecule systems.

The photochemical pathways followed by oxoacids are robust and readily generalizable to the series of molecules under study here. While, for example, the Norrish Type II reaction pathway is accessible for the longer-tailed oxoacids, it is remarkable how consistent the generated photoproducts are across alkyl tail lengths. Although, within the photochemical framework there are many constitutional isomers possible for the R,R-DHO acids generated by Scheme 4 for the longer-tailed species, which we cannot distinguish within the scope of this study, it is remarkable how well a relatively simple mechanistic framework can describe the observed photochemistry. For each ROA under study, almost all significant ions that are observed in the MS corresponding to oligomeric species can be identified in this way, with only a few minor ions escaping classification. One might expect that as the molecules under study are increased in size, the complexity of the observed products would also increase. This is, however, not the case. If anything, the observed MS are “cleaner” than those of pyruvic acid under similar reaction conditions.⁶⁷ This could be because of the surface partitioning of longer-tailed species during mass spectrometry analysis, which is biased toward observation of the more surface-active species, a bias that increases with the longer alkyl tail of the starting oxoacid. Or, it could be because of the steric effects of the oligomerization process cutting off further reaction channels that produce minor products.

Properties of Generated Photoproducts. The major products, the tartaric acid derivatives and DHO acids, are interesting because they are molecules with chiral centers that have been produced from achiral starting materials. The tartaric acid derivatives produced, R,R-tartaric acid and R-methyl-tartaric acid, have two chiral centers. For the double-tailed, R,R-tartaric acid molecules, one of the three stereoisomers produced is a meso isomer; however, in the case of the R-methyl-tartaric acid molecules and the mixed HOTA molecule, there is no meso isomer. In the case of the DHO acids, for oxoacids larger than pyruvic acid, there are always at least two chiral centers on each molecule, with the potential for three. The molecules generated are almost certainly a racemic mixture of all of the possible isomers. However, as has been noted in the literature, enantioselective environments may be able to generate an optically active product mixture.^{105–108}

The abiotic production of chiral molecules under environmentally relevant conditions points to the importance of understanding the sources of chiral molecules in the modern environment. The SML and the surfaces of aerosols have been shown to contain chiral molecules, including lipids,¹⁰⁹ but these are almost always assumed to be biotic in origin.^{14,26,27} However, as demonstrated here, it is possible to make chiral molecules in high yields from very simple, achiral precursors, suggesting that the potential for abiotic environmental sources of chirality should not be discounted.

During photolysis, oligomeric photoproducts with two and three alkyl chains are generated from single-chained ROA species. These multi-tailed amphiphilic products will likely have more surface activity than starting material, as has been shown for OOA.⁵² The increase in surface activity during photolysis also translates to a reduction in the critical aggregation concentration. Each of the oxoacids is observed to undergo self-assembly, forming aggregates that scatter light and turn the solutions visibly cloudy. For OHA, OOA, and the mixed solutions of OOA and ODA, the aggregates were characterized using DLS, and found to be monodisperse and uniform, with

sizes ranging from ~150 to ~250 nm in diameter, depending on the ROA (Table 4). This aggregation behavior has been

Table 4. Average Sizes of Aggregates Observed by Dynamic Light Scattering

ROA	avg observed diameter (nm) ^a
OHA	250 ± 20
OOA	160 ± 20
mixed OOA/ODA	150 ± 10

^aUncertainty is expressed as a 95% confidence interval.

previously reported for OOA, with microscopy indicating a spherical morphology.⁵² However, even the very short-chained OHA is observed to assemble into such aggregates, with an average size of ~250 nm in diameter, larger than the ~160 nm observed for OOA. Prior to photolysis, the precursor oxoacids do not form aggregates, as confirmed by DLS, and are below their critical aggregation concentration (except for, perhaps, ODDA), but as the photolysis proceeds, generating multi-tailed oligomeric species, aggregation is observed, even at 1 mM initial starting concentrations, for all oxoacids. The generated oligomers, therefore, have much lower critical aggregation concentrations than the starting material, as would be expected for multi-tailed species.¹¹⁰

The diameters of the aggregates observed here for OHA, OOA, and the mixed OOA:ODA are too large to be simple micelles, and the monodispersity in their size indicates ordered aggregation. It has previously been speculated that the aggregates observed for OOA may be vesicles,⁵² and the observed decrease in size as a function of increasing tail length is also suggestive that these aggregates are vesicles. The ratio of headgroup size to alkyl tail length is quite large for the oligomeric species generated from the photolysis of OHA, corresponding to a larger packing parameter¹¹¹ than for the longer tail-length oligomers. The packing parameter for the multi-tailed lipids generated from the photolysis of each of the alkyl oxoacids studied here is likely near one, a regime that generally is associated with bilayer formation.¹¹¹ If bilayers are formed, species with a higher packing parameter generally assemble into lower curvature, larger structures, which is consistent with the trend in size of aggregate observed here.

CONCLUSIONS

We have shown that the photochemical reaction mechanisms for α -keto acids in aqueous solution are readily generalizable to a series of molecules with differing alkyl chain lengths. Differences in reactivity due to chain length might be expected, but for all of the oxoacids under study here the chemical reactivity between molecules is surprisingly consistent, although a new intramolecular Norrish Type II pathway is accessible for alkyl oxoacids with a γ -CH₂ group that is not available to the shorter pyruvic acid.

Even a simple starting solution of a single alkyl oxoacid species becomes a complex mixture of oligomeric species upon photolysis. This is due in large part to the formation of reactive intermediate species with the same α -keto functionality, including pyruvic acid and parapyruvic acid derivatives. These species also undergo photochemistry, and the organic radicals generated from each of the oxoacids can react indiscriminately with each other in aqueous solution. For processes that form radicals on the alkyl chain of an oxoacid, it is likely that hydrogen abstraction occurs at multiple sites along the alkyl

chain, allowing for the formation of several constitutional isomers with the same chemical formula that cannot be distinguished from each other via the MS analysis conducted here. However, despite this, the products are not intractable as the majority of the observed species can be readily identified using simple mechanistic schemes.

The oligomers formed from this photochemistry are amphiphiles, many of which have two or three alkyl chains. The generation of chiral, multi-tailed species with increased surface activity and their subsequent self-assembly into monodisperse, spherical aggregates has important environmental implications both for today and for the early Earth.⁴ In the modern environment, this chemistry may contribute to the abiotic processes by which surface-active species are formed at the sea surface microlayer.²⁹ Prebiotically, the photochemical reactions of alkyl oxoacids are one of the only demonstrated processes by which multi-tailed lipids can be formed simply and in relatively high yields from prebiotically relevant starting materials. The properties of these multi-tailed lipids, as well as their propensity to self-assemble into ordered aggregates shown here, demonstrate their potential importance in the generation of primitive enclosures.

AUTHOR INFORMATION

Corresponding Author

*vaida@colorado.edu

ORCID 

Garret M. Miyake: 0000-0003-2451-7090

Veronica Vaida: 0000-0001-5863-8056

Present Address

[‡]Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, People's Republic of China.

Notes

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